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(71) Applicant  
Fuji Photo Film Co Ltd.,  
(Japan),  
No 210 Nakanuma,  
Minami Ashigara-shi,  
Kanagawa,  
Japan.  
(72) Inventors  
Nobuo Furutachi,  
Yoshinori Yoshida.  
(74) Agent and/or Address for  
Service  
Gee & Co.,  
Chancery House,  
Chancery Lane,  
London WC2A 1QU.

(54) Color photographic silver halide material containing a two-equivalent magenta coupler

(57) Color photographic light-sensitive material contains a silver halide emulsion layer containing a 1H-pyrazolo-[3.2-C]-S-triazole type of two-equivalent magenta coupler having at the coupling-off site a releasable group of the general formula (I):



wherein A<sub>1</sub> and A<sub>2</sub> are alkyl, aryl, hetero cyclic, acyl, sulfonyl, carbamoyl, sulfamoyl, alkoxycarbonyl or aryloxy carbonyl or they together complete an optionally fused ring, and A<sub>1</sub> or A<sub>2</sub> can be H; The triazole and pyrazole rings may have other substituents.

These couplers have good solubility in high boiling organic solvents.

The photographic material has superior color-forming rate and maximum color density.

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## SPECIFICATION

## Color photographic silver halide light-sensitive material

5 The present invention relates to a color photographic silver halide light-sensitive material (hereinafter sometimes referred to merely as a "light-sensitive material") containing novel 1H-[3.2-C]-S-triazole derivatives. More particularly, it is concerned with a light-sensitive material containing a 1H-pyrazolo[3.2-C]-S-triazole type coupler, a two-equivalent magenta coupler containing a new type of group to be released on coupling at the coupling active site thereof. 5

10 It is well known that when a color photographic silver halide light-sensitive material is color developed, an oxidized aromatic primary amine-based color developing agent reacts with a coupler to form dyes such as indophenol, indoaniline, indamine, azomethine, phenoxazine, and phenazine, producing color images. Of these color images, a magenta image is formed using 5-pyrazolone, cyanoacetophenone, indazolone, pyrazolobenzimidazole and pyrazolotriazole-based couplers. 10

15 The 5-pyrazolones are among the magenta image-forming couplers which have heretofore been most widely used and extensively studied. It is also known that dyes formed using such 5-pyrazolone-based couplers are superior in fastness against heat and light, but exhibit an unnecessary absorption having a yellow component at about 430 nm, causing color mixing. A number of magenta image-forming coupler skeletons have been proposed to reduce the color component, including a pyrazolobenzimidazole skeleton described in British Patent No. 1,047,612, an indazolone skeleton described in U.S. Patent 3,770,447, and a pyrazolotriazole skeleton described in U.S. patent 3,725,067. 15 20

Azomethine dyes formed using 1H-pyrazolo [3.2-C]-S-triazole type couplers as described in U.S. Patent 3,725,067, British Patent Nos. 1,252,418, 1,334,515 and 139,897 exhibit less unnecessary absorption at about 430 nm in a solvent, e.g., ethyl acetate, and are superior in sharp cutting properties at the long wavelength side. These couplers, however, suffer from various disadvantages. For example, their solubility in high boiling organic solvents (e.g., tricresyl phosphate and dibutyl phthalate) as used in the oil protect process is seriously low. The oil protect process is a technique well known to one skilled in the art, which is employed for the introduction of couplers in making photographic films. Moreover, they have a low color-forming rate even when passed through the usual color-forming developing bath and do not exhibit a high maximum color density. 25 30

An object of the invention is to provide a color photographic silver halide light-sensitive material containing a novel photographic two-equivalent magenta coupler which is superior in both its color-forming rate and maximum color density, and which exhibits an improved solubility in high boiling organic solvents.

It has been found that the object can be attained by using a two-equivalent magenta coupler which is of the 1H-pyrazolo[3.2-C]-S-triazole type and contains a coupling-off group represented by the general formula (I) as described hereinafter, at a site where it undergoes a coupling reaction with an oxidized product of a developing agent. 35

The present invention relates to a color photographic silver halide light-sensitive material characterized by containing a specific two-equivalent coupler of the 1H-pyrazolo[3.2-C]-S-triazole type and contains a group represented by the general formula (I) as described hereinafter as a coupling-off group at a site where it undergoes a coupling reaction with an oxidized product of a developing agent. 40

The two equivalent coupler as used herein is of the 1H-pyrazolo [3.2-C]-S-triazole type (the 1H-pyrazolo[3.2-C]-S-triazole skeleton is known as described in U.S. Patent 3,725,067) and contains a group represented by the general formula (I):

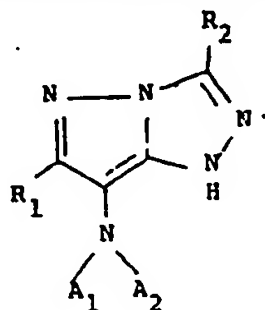
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$$\begin{array}{c} \text{A}_1 \\ \diagup \\ -\text{N} \\ \diagdown \\ \text{A}_2 \end{array}$$

50 wherein A<sub>1</sub> and A<sub>2</sub> independently represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an acyl group, a sulfonyl group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group or an aryloxycarbonyl group, provided both of A<sub>1</sub> and A<sub>2</sub> are not hydrogen atoms simultaneously; A<sub>1</sub> and A<sub>2</sub> may combine together with a nitrogen atom to form a 5- or 6-membered ring, which may be further condensed to a benzene ring or a heterocyclic ring. 50

55 This coupling-off group is located at a site where the coupler undergoes a coupling reaction with an oxidized product of a developing agent and is released on coupling. 55

Of the couplers as used herein, those compounds represented by the general formula (II) as described below are preferred.

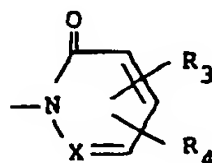


wherein A<sub>1</sub> and A<sub>2</sub> independently represent  
a hydrogen atom,

- an alkyl group (preferably an alkyl group, containing from 1 to 22 carbon atoms, such as methyl group, an ethyl group, a butyl group, an octyl group, a 2-ethylhexyl group, and an alkyl group substituted with a halogen atom, a hydroxyl group, a cyano group, an aryl group, a carboxyl group, an alkoxy group, an aryloxy group, an acylamino group, a sulfonamido group, an imido group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a ureido group, an acyl group, an alkylamino group or an arylamino group),
- an aryl group (preferably an aryl group containing from 6 to 32 carbon atoms, such as a phenyl group, a naphthyl group, and an aryl group which may be substituted with the groups described as the substituents for the foregoing alkyl group),
- a heterocyclic group (e.g., a 2-pyridyl group, a 1-quinolyl group, a 2-benzothiazolyl group, a 2-furyl group and a 2-pyrimidinyl group),
- an acyl group (preferably an acyl group containing 1 to 22 carbon atoms, e.g., an acetyl group, a butanoyl group, a hexanoyl group, a trifluoroacetyl group, a heptafluorobutanoyl group, a benzoyl group, a naphthoyl group, a pentafluorobenzoyl group, a pentachlorophenyl group, a 2-furancarboxyl group, and a 2-quinolinecarbonyl group),
- a sulfonyl group (e.g., a methanesulfonyl group, a hexanesulfonyl group, a benzenesulfonyl group, a naphthalenesulfonyl group, and an alkanesulfonyl or arylsulfonyl group which may be substituted with the groups as described for the above-described alkyl group),
- a carbamoyl group (e.g., an N-methylcarbamoyl group, an N-dodecylcarbamoyl group, an N,N-diethylcarbamoyl group, an N-phenylcarbamoyl group, and an N-alkylcarbamoyl group, N,N-dialkylcarbamoyl group, N-arylcarbamoyl group, or N,N-diarylcarbamoyl group which may be substituted with the groups as described for the above-described alkyl group),
- a sulfamoyl group (e.g., an N-methylsulfamoyl group, an N-n-octylsulfamoyl group, an N-phenylsulfamoyl group, an N,N-diethylsulfamoyl group, and an N-alkyl-sulfamoyl group, N,N-dialkylsulfamoyl group, N-arylsulfamoyl group, or N,N-diarylsulfamoyl group which may be substituted with the groups as described for the above-described alkyl group), or
- an alkoxycarbonyl group (e.g., a methoxycarbonyl group, a butyloxycarbonyl group, a dodecyloxycarbonyl group, a 2-ethylhexyloxycarbonyl group, and an alkoxycarbonyl group which may be substituted with the groups described for the alkyl group), provided both of A<sub>1</sub> and A<sub>2</sub> are not hydrogen atoms simultaneously.
- A<sub>1</sub> and A<sub>2</sub> may combine together in combination with a nitrogen atom to form a 5- or 6-membered ring. These 5- and 6-membered rings include:
- an aromatic heterocyclic ring containing a nitrogen atom and constituting a 6  $\pi$  or 10  $\pi$  electron system (e.g., a 1-pyrrolyl group, a 1-imidazolyl group, a 1-pyrazolyl group, a 1-(1,2,4-triazolyl group), a 1-(1,2,3-triazolyl group), a 1-(1,2,3,4-tetrazolyl group), a 1-(1,2,3,5-tetrazolyl group), a 1-indolyl group, a 2-isoindolyl group, a 1-benzimidazolyl group, a 1-benzotriazolyl group, and an aromatic heterocyclic group in which the foregoing aromatic heterocyclic group may be substituted with a halogen atom, a cyano group, a nitro group, an alkyl group, an aryl group, a carboxyl group, an alkoxy group, an aryloxy group, an acylamino group, a sulfonamido group, an imido group, an alkoxycarbonyl group, an aryloxycarbonyl group, an alkylthio group, an arylthio group, an alkylsulfonyl group, an arylsulfonyl group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, a ureido group, an acyl group, an alkylamino group or an arylamino group),
- a saturated or unsaturated heterocyclic group containing a nitrogen atom, but not forming an aromatic ring (e.g., a 1-pyrrolidinyl group, a 1-piperidinyl group, an N-morpholinyl group, an N-1,2,3,4-tetrahydroquinolyl group, a 1-pyrrolinyl group, a 1-imidazolinyl group, a 1-pyrazolidinyl group, a 2-isoindolinyl group, a 1-indolinyl group, and a heterocyclic group in which the foregoing saturated or unsaturated heterocyclic group is substituted with the substituents as described for the foregoing aromatic heterocyclic group),
- a cyclic imido group (e.g., an N-succinic acid imido group, an N-phthalimido group, a 1-N-hydantoinyl group, a 3-N-2,4-dioxo-oxazolidinyl group, a 4-N-urazolyl group, and an imido group in which the foregoing

imido group is substituted with the substituents as described for the foregoing aromatic heterocyclic group),  
 a 2-N-1,1-dioxo-3-(2H)-oxo-1,2-benzisothiazolyl group (saccharin),  
 a 2-N-1,1-dioxo-3-(2H)-oxo-1,2-benzisothiazolyl group which may contain the substituents as described for  
 the foregoing aromatic heterocyclic group,  
 5 a group represented by the formula: 5

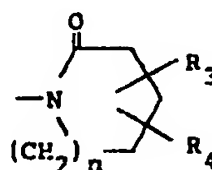
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(wherein X is  $-\text{CH}=\text{}$  or  $-\text{N}=\text{}$ , and  $\text{R}_3$  and  $\text{R}_4$  independently represent a hydrogen atom, or may contain the  
 substituents as described for the foregoing aromatic heterocyclic group;  $\text{R}_3$  and  $\text{R}_4$  may combine together to  
 15 form a condensed ring (preferred examples of which are a 2(1H)-pyridone group and a phthalazinedione  
 group), and 15  
 a group represented by the formula:

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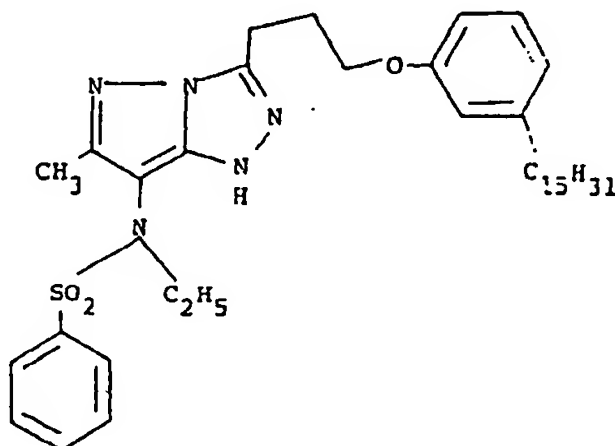


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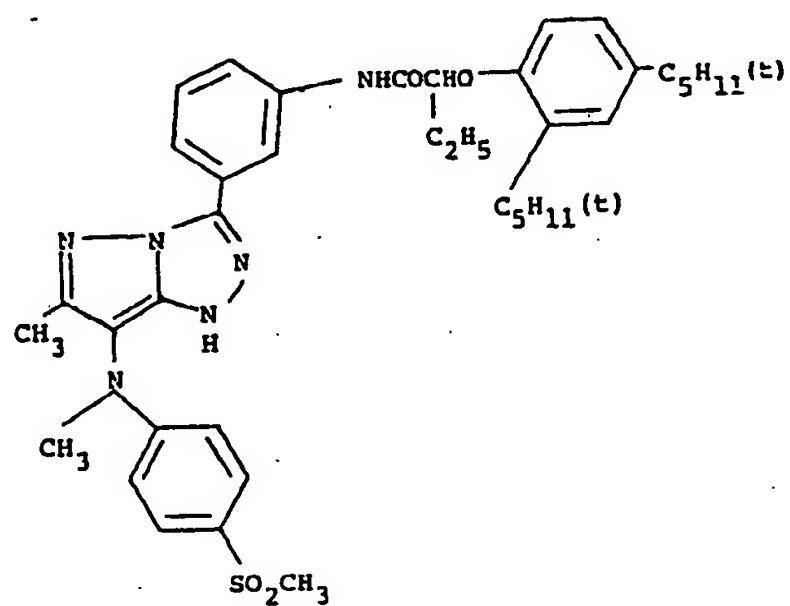
(wherein  $n$  is 1 or 2, and  $\text{R}_3$  and  $\text{R}_4$  independently represent a hydrogen atom, or may contain the  
 substituents as described for the foregoing aromatic heterocyclic group;  $\text{R}_3$  and  $\text{R}_4$  may combine together to  
 form a condensed ring (preferred examples of which are a 2-oxo-1-pyrrolidinyl group and a 2-oxo-1-  
 piperidinyl group). 25

In the general formula (II),  $\text{R}_1$  and  $\text{R}_2$  may be the same or different, and independently represent  
 30 a hydrogen atom, 30  
an alkyl group (e.g., a methyl group, a propyl group, a tert-butyl group, a hexadecyl group, a  
2-(2,4,6-trichlorophenyl)ethyl group, a 3-(3-pentadecylphenoxy)propyl group, a 3-(2,4-di-tert-  
amylphenoxy)propyl group, or a 2-[ $\alpha$ -(3-tert-butyl-4-hydroxyphenoxy)tetradecanamidoethyl]group),  
an aryl group (e.g., a phenyl group, an  $\alpha$ - or  $\beta$ -naphthyl group, a 4-methylphenyl group, a  
 35 2,4,6-trichlorophenyl group, a 4-[ $\alpha$ -(2,4-di-tert-amylphenoxy)butyramido]phenyl group or a 4-[ $\alpha$ -(3-tert-butyl- 35  
4-hydroxyphenoxy)tetradecanamido]-2,6-dichlorophenyl group),  
a heterocyclic group (e.g., a pyridyl group, a thienyl group or a quinolyl group),  
an acylamino group (e.g., an acetylamino group, a benzamido group, a 3-(2,4-di-tert-amylphenoxy)-  
butyramido group or a 3-(3-pentadecylphenoxy)butyramido group),  
 40 an alkylamino group (e.g., a methylamino group, a diethylamino group or a  $n$ -dodecylamino group), 40  
an anilino group (e.g., a phenylamino group, a 2-chloro- $t$ -tetradecanamidophenylamino group or a  
4-[ $\alpha$ -(3-tert-butyl-4-hydroxyphenoxy)tetradecanamido]anilino group),  
an alkoxy carbonyl group (e.g., a methoxycarbonyl group or a tetradecyloxycarbonyl group), and  
an alkylthio group (e.g., a hexylthio group or a dodecylthio group),  
 45 provided both of  $\text{R}_1$  and  $\text{R}_2$  are not hydrogen atoms. 45  
 Typical examples of the magenta couplers as used herein are given below.

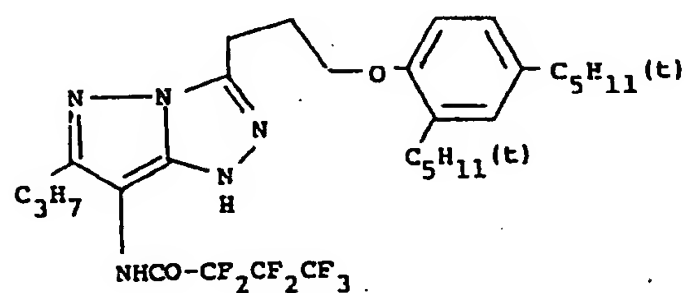
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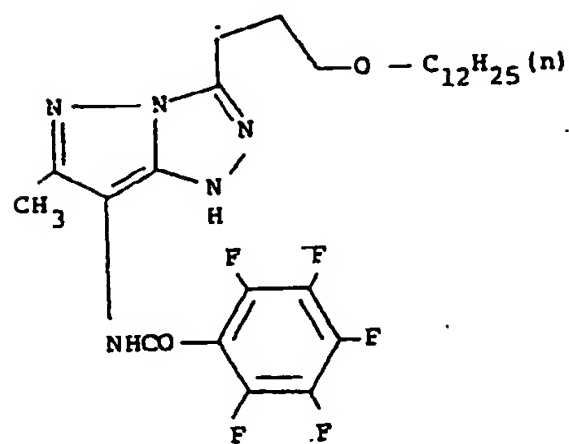
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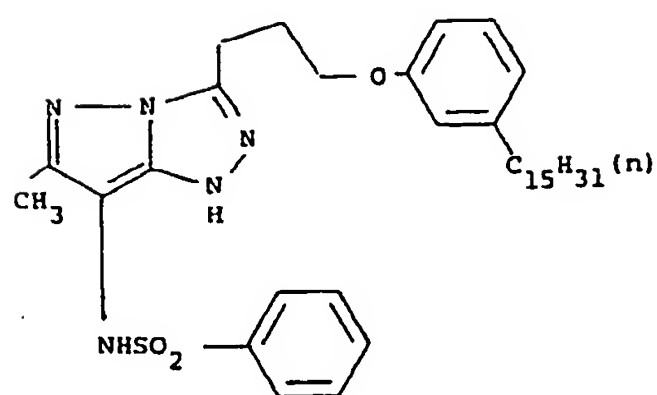
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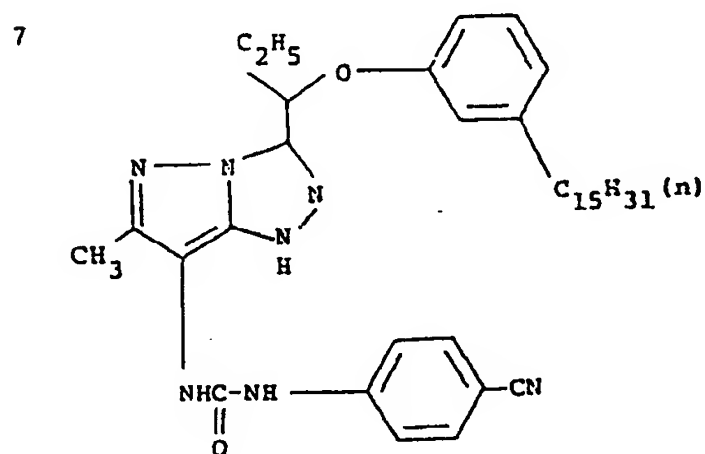
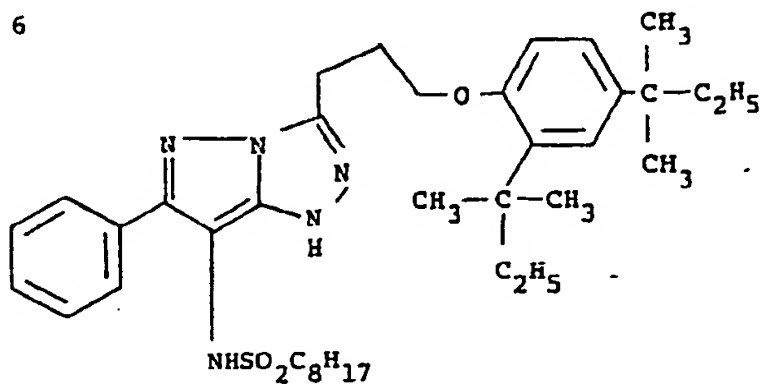


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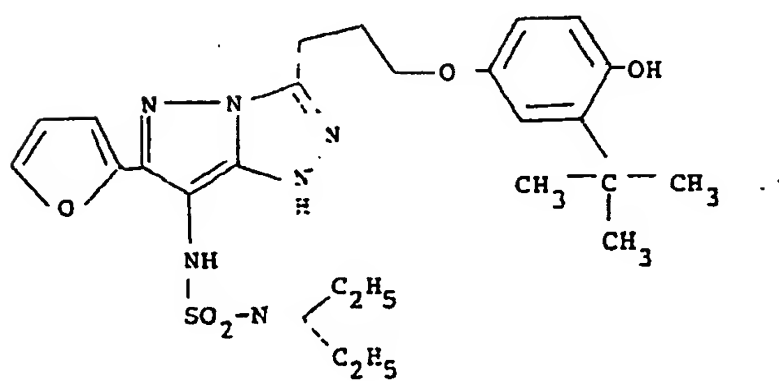


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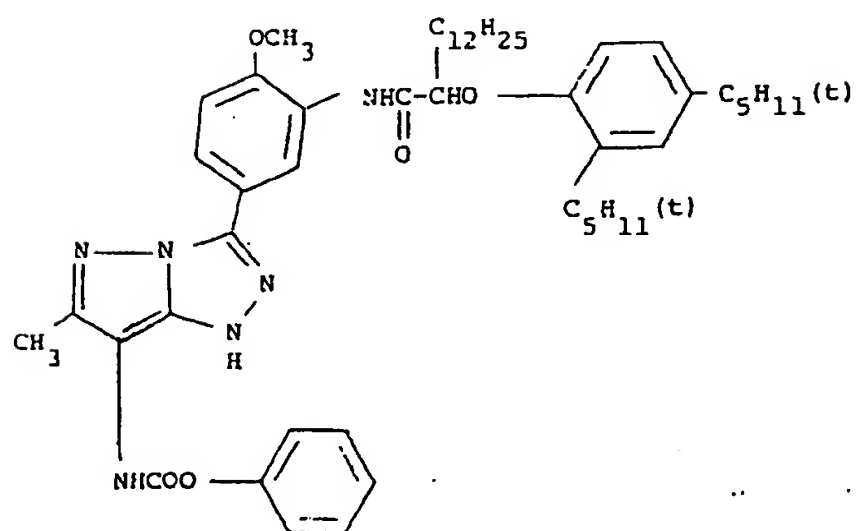




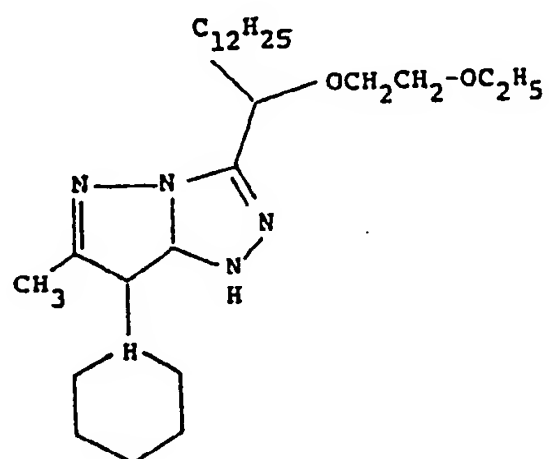
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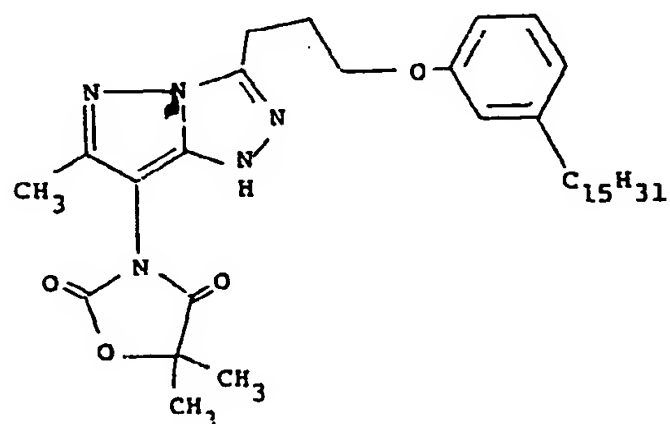
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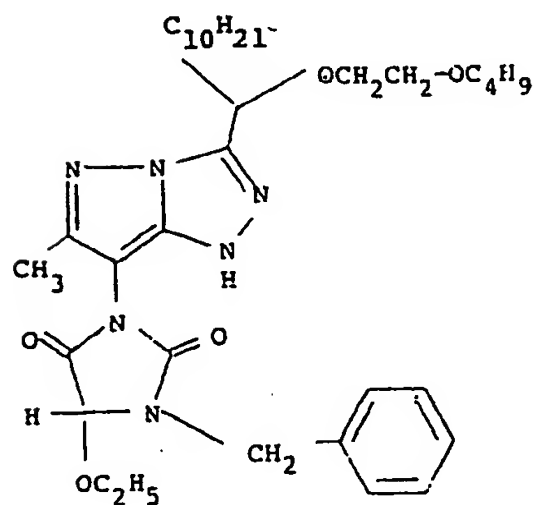
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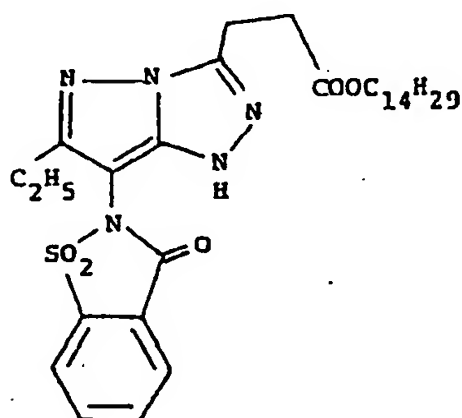
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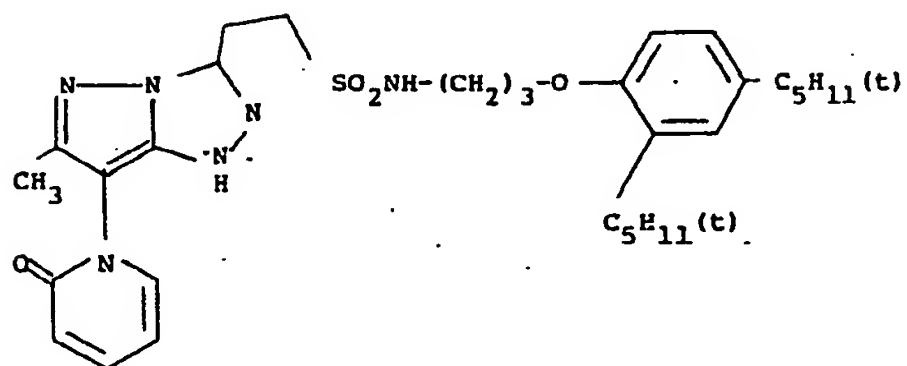
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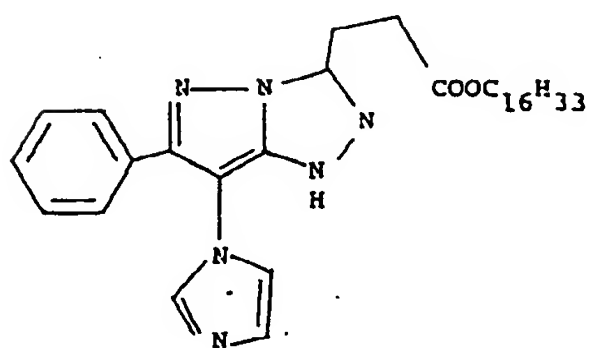
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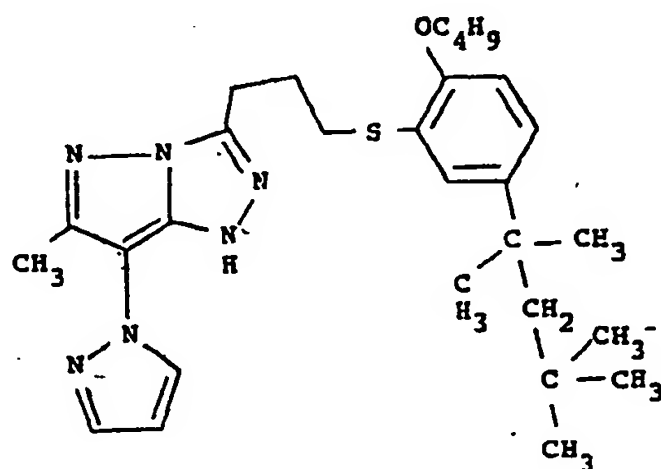


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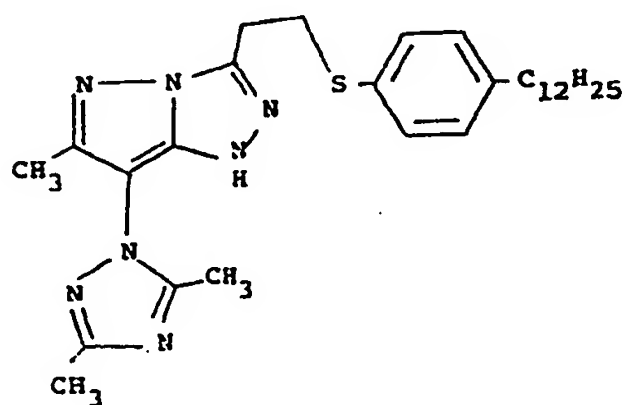




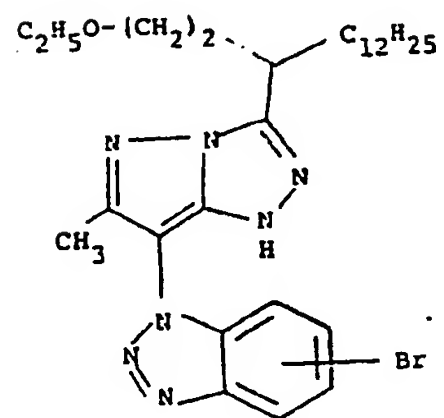
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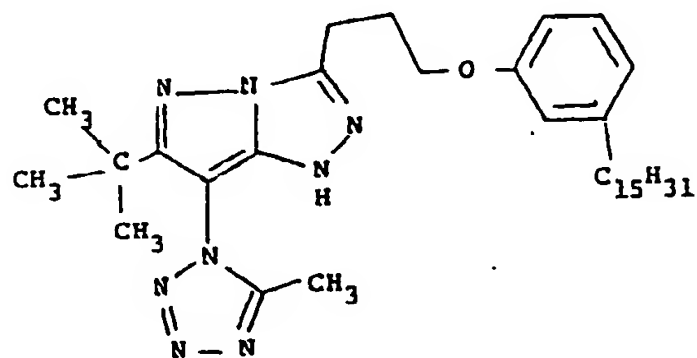
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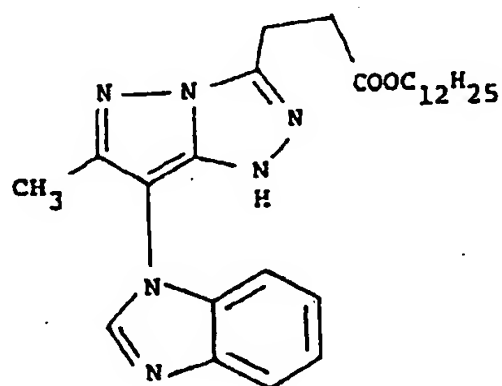
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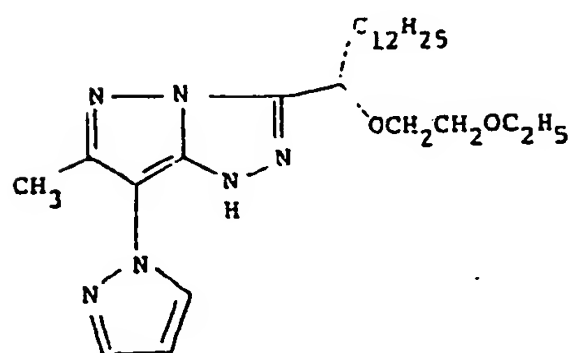
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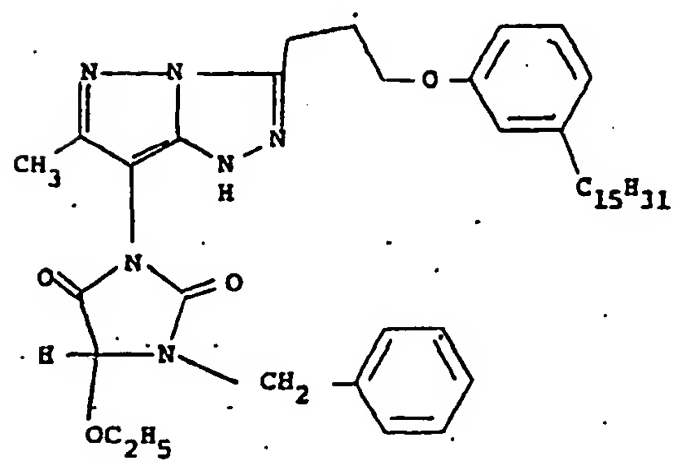
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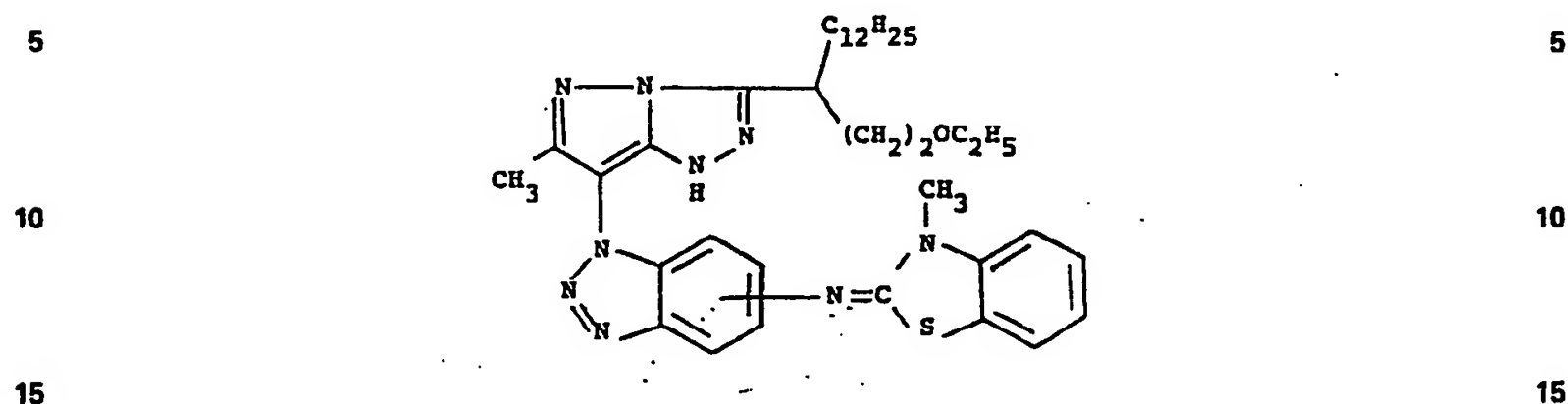
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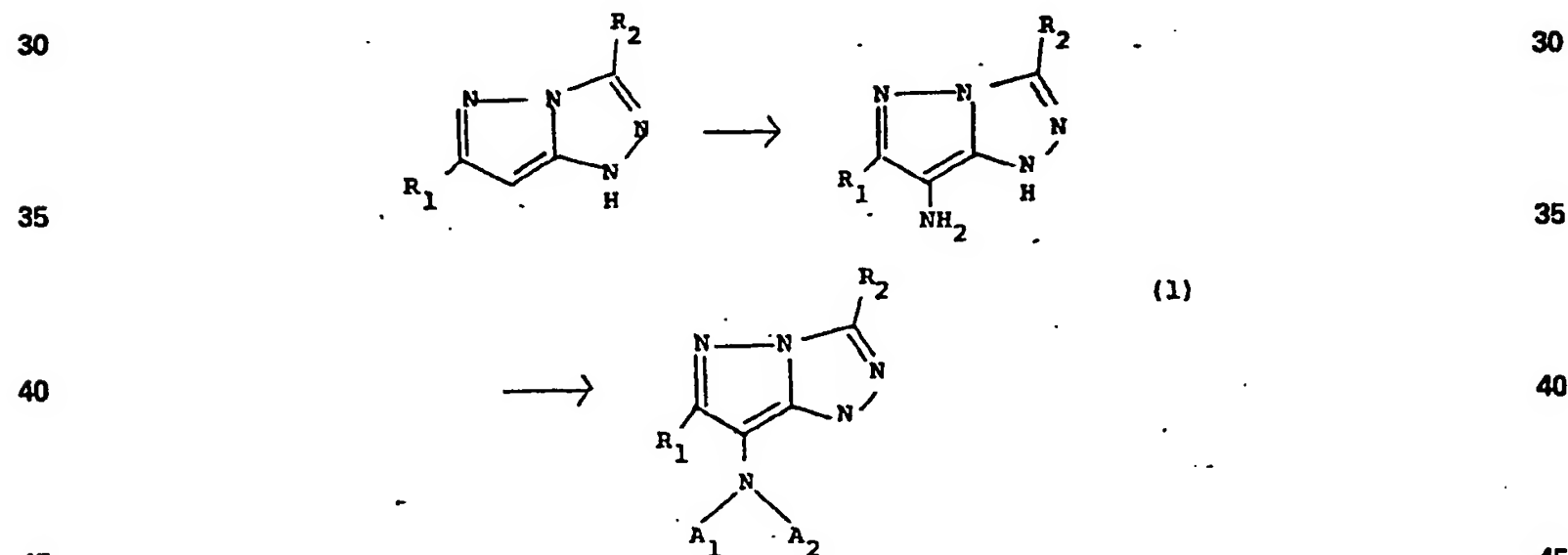
Of the couplers represented by the general formula (II), those compounds are especially preferred in which  $A_1$  and  $A_2$  of the general formula (I) combine together to form a 5- or 6-membered ring, or a heterocyclic ring resulting from condensation of the 5- or 6-membered ring and a benzene ring. These compounds exhibit excellent performance in achieving the object of the invention.

The amount of the magenta coupler used is usually from  $2 \times 10^{-3}$  to  $5 \times 10^{-1}$  mol, preferably from  $1 \times 10^{-2}$  to  $5 \times 10^{-1}$  mol, per mol of silver.

Typical methods of preparation of the couplers as used herein are described below.

The 1H-pyrazolo [3.2-C]-S-triazole skeleton and the ballast group can be prepared by the methods described in British Patent 1,252,418 and U.S. Patent 3,705,896.

(1) A method in which an amino group is introduced in the coupling active site, and the amino group thus introduced is then modified, is illustrated by the following process (1):

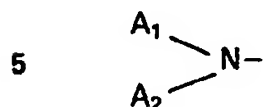


The amino group can be easily introduced in the coupling active site by the method described in U.S. Patent 3,419,391; i.e., nitrosation is caused to occur at the coupling active site using a suitable nitrosating agent, e.g., sodium nitrite or isoamyl nitrite, and the thus-prepared nitroso group is reduced in a suitable manner, such as by a hydrogen addition method in which it is contacted with hydrogen gas in the presence of a palladium carbon catalyst, or a chemical reduction method using stannous chloride, for example.

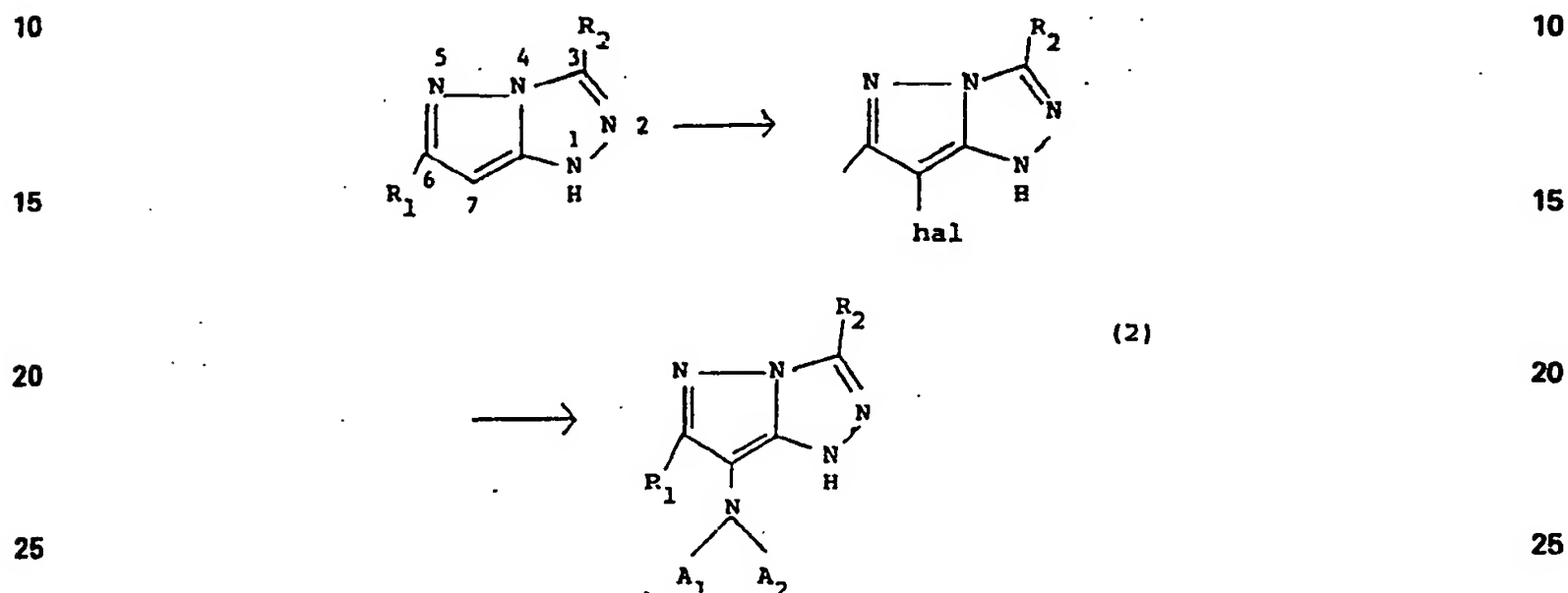
Modification of the above-prepared amino group results in the formation of those compounds in which  $A_1$  and  $A_2$  are each an acyl group, a sulfonyl group, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group or an aryloxy carbonyl group. This modification can be performed by reacting the amino compound with  $A_1$ -hal or  $A_2$ -hal (wherein  $A_1$  and  $A_2$  are as described for the general formula (I), and the symbol "hal" represents a halogen atom, e.g., a chlorine atom or a bromine atom) at a temperature of from 0 to 100°C in a solvent inert to the  $A_1$ -hal, such as acetic acid, methylene chloride, chloroform, benzene, pyridine, dimethylformamide, dimethylsulfoxide or acetonitrile. In performing this reaction, it is preferred to use a suitable dehydrohalogenation agent (e.g., triethylamine, diazabicyclo[2.2.2]octane, and sodium acetate).

This method provides Couplers Nos. 3, 4, 5, 6, 7, 8 and 9.

(2) A method in which a halogen atom is introduced in the coupling active site, and the halogen atom thus introduced is replaced by the group

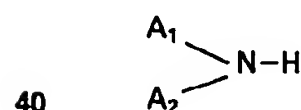


is illustrated by the following process (2):



Introduction of the halogen atom (e.g., a chlorine atom and a bromine atom in the coupling active site, i.e., the 7-position, of the 1H-pyrazolo[3,2-C]-S-triazole skeleton can be conducted by the method as described in U.S. Patent 3,725,067 using a suitable halogenation agent, such as sulfonyl chloride, chlorine gas, bromine, N-chlorosuccinimide or N-bromosuccinimide.

The replacement of the halogen atom results in the formation of those compounds in which A<sub>1</sub> and A<sub>2</sub> are each an alkyl group, an aryl group, a heterocyclic group, or combine together in combination with a nitrogen atom, forming a 5- or 6-membered ring. This replacement can be performed by dissolving the above-prepared halogen-substituted compound and



in an alcohol solvent (e.g., ethanol or isopropyl alcohol), an aprotic polar solvent (e.g., dimethylformamide, sulfolane or hexamethylphosphotriamide), or a halogenated hydrocarbon solvent (e.g., methylene chloride or chloroform), and reacting them in the presence of a suitable base (e.g., triethylamine, sodium hydroxide, potassium hydroxide, diazabicyclo[2.2.2]octane or anhydrous potassium carbonate) (refer to Japanese Patent Publication No. 45135/81).

This method provides Couplers Nos. 1, 2, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22 and 23.

The 6  $\pi$  or 10  $\pi$  electron system nitrogen-containing aromatic heterocyclic ring can be introduced by the method as described in Japanese Patent Publication No. 36577/82; that is, the heterocyclic compound is added to the halogen-substituted compound in an amount of at least two moles per mole of the halogen-substituted compound, and they are reacted by heating at 50 to 150°C in the absence of solvents or by heating at 30 to 150°C in an aprotic solvent (e.g., dimethylformamide, sulfolane, and hexamethylphosphotriamide).

This method provides Couplers Nos. 15, 16, 17, 18, 19 and 20.

In addition to the couplers of the invention, dye-forming couplers, i.e., compounds capable of forming color by oxidative coupling with aromatic primary amine developers (e.g., phenylenediamine derivatives and aminophenol derivatives) at a step of color development, as described below can be used.

For example, magenta couplers such as a 5-pyrazolone coupler, a pyrazolobenzimidazole coupler, a cyanoacetylcumarone coupler, and an open-chain acylacetone coupler, yellow couplers such as an acylacetamide coupler (e.g., benzoylacetylacetanilides and pivaloylacetylacetanilides), cyan couplers such as a naphthol coupler, and phenol couplers can be used.

It is desirable for these couplers to contain a hydrophobic group called a ballast group, i.e., be non-diffusing, or to be a polymerized form. The couplers may be either four equivalent or two equivalent relative to silver ion. Moreover, they may be color couplers having the action of color correction, or

couplers (so-called DIR couplers) releasing a development inhibitor with development.

Besides DIR couplers, colorless DIR coupling compounds providing a colorless coupling reaction product and releasing a development inhibitor can be used.

To satisfy characteristics required for a light-sensitive material, two or more types of couplers as described above can be used in the same layer, or the same compound can be used in two or more layers. 5

The couplers can be introduced in a silver halide emulsion layer by any suitable known techniques, such as the method as described in U.S. Patent 2,322,027. A typical method of introduction involves dissolving the coupler in a suitable solvent, such as phthalic acid alkyl esters (e.g., dibutyl phthalate and dioctyl phthalate), phosphoric esters (e.g., diphenyl phosphate, triphenyl phosphate, tricresyl phosphate, and dioctylbutyl phosphate), citric acid esters (e.g., tributyl acetyl citrate), benzoic acid esters (e.g., octyl benzoate), 10 alkylamides (e.g., diethyl laurylamide), aliphatic acid esters (e.g., dibutoxyethyl succinate and diethyl azelate), and trimesic acid esters (e.g., tributyl trimesate), and organic solvents having a boiling point of from about 30 to 150°C, for example, lower alkyl acetate (e.g., ethyl acetate and butyl acetate), ethyl propionate, sec-butyl alcohol, methyl isobutyl ketone,  $\beta$ -ethoxyethyl acetate, and 2-methoxy ethyl acetate, and 15 thereafter, dispersing the resulting solution in hydrophilic colloid. 15

The high boiling and low boiling organic solvents as described above can be used in combination with each other.

The dispersion method using polymerized products as described in Japanese Patent Publication No. 39853/76 and Japanese Patent Application (OPI) No. 59943/76 (the term "OPI" as used herein means a 20 "published unexamined Japanese patent application") can also be used. 20

The coupler is introduced in the hydrophilic colloid as an alkaline aqueous solution when it contains an acid group such as carboxylic acid and sulfonic acid.

It is convenient for the photographic color former as used herein to be chosen so that an image of intermediate scale can be obtained. It is preferred that the maximum absorption band of cyan dye formed 25 from a cyan color former be present between about 600 and 720 nm, the maximum absorption band of magenta dye formed from a magenta color former, between about 500 and 580 nm, and the maximum absorption band of yellow dye formed from a yellow color former, between about 400 and 480 nm. 25

In the practice of the present invention, known discoloration inhibitors as described below can be used in combination. Color image stabilizers as used herein can be used singly or in combination with each other.

30 Known discoloration inhibitors include hydroquinone derivatives as described in, for example, U.S. Patents 2,360,290, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 2,728,659, 2,732,300, 2,735,765, 2,710,801 and 2,816,028, and British Patent 1,363,921, gallic acid derivatives as described in, for example, U.S. Patents 3,457,079 and 3,069,262, *p*-alkoxyphenols as described in U.S. Patents 2,735,765 and 3,698,909, and Japanese Patent Publication Nos. 20977/74 and 6623/77, *p*-oxyphenol derivatives as described in U.S. 35 Patents 3,432,300, 3,573,050, 3,574,627 and 3,764,337, Japanese Patent Applications (OPI) Nos. 35633/77, 147434/77 and 152225/77, and bisphenols as described in U.S. Patent 3,700,455. 35

The light-sensitive material of the invention may contain, as anti-colorfoggants, hydroquinone derivatives, aminophenol derivatives, gallic acid derivatives, ascorbic acid derivatives, etc. Examples are described in, for example, U.S. Patents 2,360,290, 2,336,327, 2,403,721, 2,418,613, 2,675,314, 2,701,197, 2,704,713, 40 2,728,659, 2,732,300 and 2,735,765, Japanese Patent Applications (OPI) Nos. 92988/75, 92989/75, 93928/75, 110337/75, and 146235/77, and Japanese Patent Publication No. 23813/75. 40

The light-sensitive material of the invention may contain water-soluble dyes as filter dyes or for various purposes, for example, prevention of irradiation in the hydrophilic colloid layer thereof.

45 Such water-soluble dyes include oxonol dyes, hemioxonol dyes, styryl dyes, merocyanine dyes, cyanine dyes and azo dyes. Of these dyes, oxonol, hemioxonol and merocyanine dyes are useful. Suitable examples of the dyes that can be used are described in British Patents 584,609 and 1,177,429, Japanese Patent Applications (OPI) Nos. 85130/73, 99620/74, 114420/74 and 108115/77, and U.S. Patents 2,274,782, 2,533,472, 2,956,879, 3,148,187, 3,177,078, 3,247,127, 3,540,887, 3,575,704, 3,653,905, 3,718,472, 4,071,312 and 4,070,352. 45

50 The photographic emulsion layer of the photographic light-sensitive material of the invention may contain polyalkyleneoxide or its ether, ester, amine or like derivatives, thioether compounds, thiomorpholines, quaternary ammonium chloride compounds, urethane derivatives, urea derivatives, imidazole derivatives, 3-pyrazolidones, etc. for the purpose of increasing sensitivity or contrast, or accelerating development. Compounds which can be used for that purpose are described in, for example, U.S. Patents 2,400,532, 55 2,423,549, 2,716,062, 3,617,280, 3,772,021 and 3,808,003, and British Patent 1,488,991. 55

The light-sensitive material of the invention may contain ultraviolet ray absorbers in the hydrophilic layer thereof. Ultraviolet ray absorbers which can be used include benzotriazole compounds substituted with an aryl group (e.g., those compounds as described in U.S. Patent 3,533,794), 4-thiazolidone compounds (e.g., compounds as described in U.S. Patents 3,314,794 and 3,352,681), benzophenone compounds (e.g., 60 compounds as described in Japanese Patent Application (OPI) No. 2784/71), cinnamic acid ester compounds (e.g., compounds as described in U.S. Patents 3,705,805 and 3,707,375), butadiene compounds (e.g., compounds as described in U.S. Patent 4,045,229, and benzooxazole compounds (e.g., compounds as described in U.S. Patent 3,700,455). In addition, the compounds as described in U.S. Patent 3,499,762 and Japanese Patent Application (OPI) No. 48535/79 can be used. Ultraviolet ray-absorbing couplers (e.g., 65  $\alpha$ -naphthol-based cyan dye-forming couplers), ultraviolet ray-absorbing polymers, etc. can also be used. 65

These ultraviolet ray absorbers may be mordanted in a specific layer.

Photographic emulsions as used herein may be subjected to spectral sensitization using methine dyes, for example. Dyes which can be used for this spectral sensitization include cyanine dye, merocyanine dye, composite cyanine dye, composite merocyanine dye, holopolar cyanine dye, hemicyanine dye, styryl dye and hemioxonol dye; especially useful are cyanine, merocyanine and composite merocyanine dyes. To these dyes are applicable all of the nuclei which are commonly utilized in cyanine dyes as basic heterocyclic nuclei. That is, a pyrroline nucleus, an oxazoline nucleus, a thiazoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus, a pyridine nucleus, etc.; nuclei resulting from the fusion of alicyclic hydrocarbon rings of the above-described nuclei; and nuclei resulting from the fusion of aromatic hydrocarbon rings to the nuclei, i.e., an indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthimidazole nucleus, a quinoline nucleus, etc. can be applied. These nuclei may be substituted at a carbon atom or atoms thereof.

In merocyanine or composite merocyanine dyes, as nuclei having the ketomethylene structure, 5 to 6-membered heterocyclic nuclei such as a pyrazoline-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidin-2,4-dione nucleus, a thiazolidin-2,4-dione nucleus, a rhodanine nucleus, and a thiobarbituric acid nucleus can be used.

Useful sensitizing dyes are described in, for example, Germany Patent 929,080, U.S. Patents 2,231,658, 2,493,748, 2,503,776, 2,519,001, 2,912,329, 3,656,959, 3,672,897, 3,694,217, 4,025,349, and 4,046,572, British Patent 1,242,588, Japanese Patent Publications Nos. 14030/69 and 24844/77.

These sensitizing dyes can be used singly or in combination with each other. They are often used in combination with each other particularly for the purpose of super-sensitization. Suitable examples are described in U.S. Patents 2,688,545, 2,977,229, 3,397,060, 3,522,052, 3,527,641, 3,617,293, 3,628,964, 3,666,480, 3,672,898, 3,679,428, 3,703,377, 3,769,301, 3,814,609, 3,837,862, and 4,026,707, British Patents 1,344,281 and 1,50,803, Japanese Patent Publications Nos. 4936/68 and 12375/78, and Japanese Patent Application (OPI) Nos. 110618/77 and 109925/77.

Dyes not having a spectral sensitization action by themselves, or substances not substantially absorbing visible light but exhibiting super-sensitization may be introduced in combination with sensitizing dyes into the emulsions. Examples are aminostyryl compounds substituted by a nitrogen-containing heterocyclic group (e.g., the compounds described in U.S. Patents 2,933,390 and 3,635,721), aromatic organic acid-formaldehyde condensates (e.g., the compounds described in U.S. Patent 3,743,510), cadmium salts, and azaindene compounds. Particularly useful ones are the combinations described in U.S. Patents 3,615,613, 3,615,641, 3,617,295 and 3,635,721.

The light-sensitive material of the invention can be processed by known techniques. In these photographic processings, known processing solutions can be used. The processing temperature is usually chosen within the range of from 18 to 50°C, but may be lower than 18°C or higher than 50°C. A developing processing (black and white photographic processing) to form a silver image or a color photographic processing comprising a developing processing to form a dye image can be applied to the light-sensitive material of the invention.

A color developer is generally an alkaline aqueous solution containing a color-forming developing agent. As such color-forming developing agents, known primary aromatic amine developers, such as phenylenediamines (e.g., 4-amino-N,N-diethylaniline, 3-methyl-4-amino-N,N-diethylaniline, 4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-hydroxyethylaniline, 3-methyl-4-amino-N-ethyl-N-β-methanesulfonamidoethylaniline and 4-amino-3-methyl-N-ethyl-N-β-methoxyethylaniline) can be used.

In addition, the compounds described in, for example, L.F.A. Mason, *Photographic Processing Chemistry*, Focal press (1966), pp. 226-229, U.S. Patents 2,193,015 and 2,592,364, and Japanese Patent Application (OPI) No. 64933/73 may be used.

The color developer can further contain pH buffers, such as sulfites of alkali metals, carbonic acid salts, boric acid salts, and phosphoric acid salts, development inhibitors, such as bromides, iodides, and organic antifoggants, and antifoggants. In addition, if desired, it may contain a hard water-softening agent, a preservative, e.g., hydroxylamine, an organic solvent, e.g., benzyl alcohol and diethylene glycol, a development accelerator, e.g., polyethylene glycol, quaternary ammonium salts, and amines, a dye-forming coupler, a competitive coupler, a foggant, e.g., sodium boron hydride, an auxiliary developer, e.g., 1-phenyl-3-pyrazolidone, a tackifier, the polycarboxylic acid-based chelating agents described in U.S. Patent 4,083,723, the anti-oxidants described in West German Patent (OLS) No. 2,622,950, etc.

After color development, the photographic emulsion layer is usually bleached. This bleaching process may be performed simultaneously with or separately from a fixing process. Bleaching agents which can be used include compounds of multi-valent metals, e.g., iron (III), cobalt (III), chromium (VI) and copper (II), peracids, quinones, and nitroso compounds. For example, ferricyanides, dichromates, organic complex salts of iron (III) or cobalt (III), aminopolycarboxylic acids, such as ethylenediaminetetraacetic acid, nitrilotriacetic acid and 1,3-diamino-2-propanoltetraacetic acid, or complex salts of organic acids such as citric acid, tartaric acid, and malic acid, persulfates, permanganates, nitrophenol, etc. can be used. Of these compounds, potassium ferri-cyanide, iron (III) sodium ethylenediaminetetraacetate, and iron (III) ammonium ethylenediaminetetraacetate are especially useful. Ethylenediaminetetraacetic acid-iron (III) complex salts are useful in both in independent bleaching solution and a monobath bleach-fixing solution.

To these bleaching or bleach-fixing solutions can be added various additives as well as the bleach

accelerators described in U.S. Patents 3,042,520 and 3,241,966, Japanese Patent Publications Nos. 8506/70 and 8836/70, and the thiol compounds described in Japanese Patent Application (OPI) No. 65732/78.

The present invention is explained in greater detail by reference to the following examples.

## 5 EXAMPLE 1

5

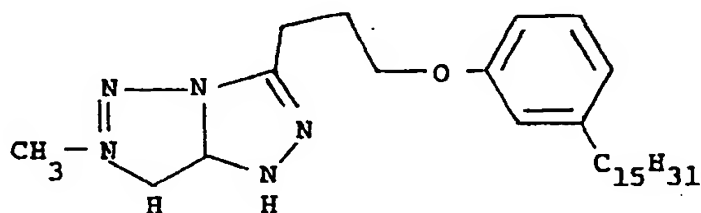
### Film A

Coupler 22, a coupler of the invention, (10 g) was dissolved in 10 ml of trioctyl phosphate and 20 ml of ethyl acetate, and the solution thus prepared was added to 100 ml of 10% gelatin containing sodium dodecylbenzene-sulfonate and emulsified by stirring by the use of a homogenizer emulsifying machine. The thus-prepared emulsion was coated on a cellulose triacetate support and dried to obtain a film. This film was good in transparency and its surface was smooth.

### Film B

A film was produced in the same manner as in Film A except that a comparative coupler, Coupler A, as shown below was used in place of Coupler 22. The transparency of the film was poor, and the surface was rough. Precipitation of Coupler A was observed. Thus it can be seen that the compound of the invention is superior in solubility and emulsion stability to the comparative coupler.

### Coupler A (Comparative Coupler)



## 35 EXAMPLE 2

35

Couplers 3, 8, 9, 16, 17 and 18, couplers of the invention, were tested in the same manner as in Film A of Example 1 for solubility and emulsion stability.

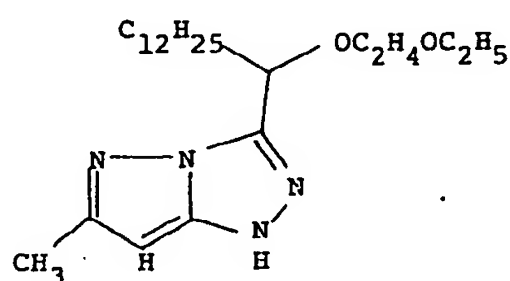
Films prepared using the couplers were good in transparency and had a smooth surface.

In addition, using emulsions which had been allowed to stand in a refrigerator for 10 days, films were prepared. These films were also of good transparency and had a smooth surface.

**EXAMPLE 3****Film C**

A comparative coupler, Coupler B, as illustrated below (8.2 g) was dissolved in 10 ml of trioctyl phosphate, 5 ml of tricresyl phosphate, and 10 ml of ethyl acetate, and the solution thus prepared was added to 100 g of a 10% aqueous gelatin solution containing sodium di-sec-butyl-naphthalenesulfonate and emulsified by stirring by the use of a homogenizer emulsifying machine to obtain an emulsion. 5

The emulsion thus obtained was mixed with 300 g of a green-sensitive silver chlorobromide emulsion (Br: 45 mol%; Cl: 55 mol%; silver content: 13.5 g), and a coating aid, sodium dodecylbenzenesulfonate, and a hardener, 2-hydroxy-4,6-dichloro-S-triazine, were added thereto. The resultant mixture was coated on a cellulose triacetate support, and a gelatin coating solution (gelatin: 1 g/m<sup>2</sup>) was coated thereon and dried to provide a protective layer. 10

**Coupler B (Comparative Coupler)****Film D**

A film was prepared in the same manner as in Film C above except that 9.3 g of Coupler 21, a coupler of the invention, and 200 g of the green-sensitive emulsion were used.

Films C and D were exposed to light at 1,000 lux/sec by means of a sensitometer and, thereafter, processed with the following solutions: 30

**Developer**

35	Benzyl alcohol	15 ml	35
	Na <sub>2</sub> SO <sub>3</sub>	5 g	
	KBr	0.4 g	
40	Hydroxylamine sulfate	2 g	40
	4-Amino-3-methyl-N-ethyl-N-[β-(methanesulfonamido)ethyl]-p-phenylenediamine	6 g	45
45	Na <sub>3</sub> CO <sub>3</sub> (monohydrate)	30 g	
	Water to make	1 liter	
50	(pH: 10.1)		50

**Bleach-Fixing Solution**

55	Ammonium thiosulfate (70 wt%)	150 ml	55
	Na <sub>2</sub> SO <sub>3</sub>	15 g	
	Na Fe(EDTA)	40 g	
60	EDTA	4 g	60
	Water to make	1 liter	
65	(pH: 6.9)		65



	<i>Processing Steps</i>	<i>Temperature (°C)</i>	<i>Times (min)</i>	
5	Development	33	3	5
	Bleach-Fixing	33	1.5	
	Rinsing	28-35	3	
10	Drying			10

After the above processing, the dye development concentration was measured by a Macbeth densitometer with a Status AA Filter. ("Macbeth" and "Status" are reg. Trademarks.)  
The results are shown in Table 1 below.

	TABLE 1			
20		<i>Film C</i>	<i>Film D</i>	20
	Coupler	B	21	
25		(comparative coupler)	(coupler of the invention)	25
	Amount of Ag Coated	700 mg/m <sup>2</sup>	466 mg/m <sup>2</sup>	
30	Amount of Coupler Coated	423 mg/m <sup>2</sup>	481 mg/m <sup>2</sup>	30
	Molar Ratio of Ag to Coupler (Ag/Coupler)	6	4	
35	Maximum Density	2.51	2.95	35

It can be seen from Table 1 that for Film D in which the coupler of the invention is used, the color density is high irrespective of the fact that the amount of silver coated is small.

## EXAMPLE 4

Films E to N were prepared in the same manner as in the preparation of Film D of Example 3 except that 200 g of a green-sensitive silver iodobromide emulsion (I: 6 mol%; Br: 94 mol%; silver content: 9 g) was used as an emulsion and as a coupler, those shown in Table 2 were used. These films were processed also in the same manner as in Example 3, and the maximum density was measured. In each case, the molar ratio of silver to coupler (Ag/cp) was adjusted to 4.

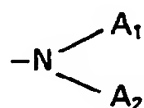
TABLE 2

<i>Film</i>	<i>Coupler</i>	<i>Maximum Density</i>
E	2	2.20
F	3	2.45
G	7	2.40
H	9	2.25
I	12	2.60
J	14	2.65
K	16	2.65
L	17	2.65
M	19	2.60
N	21	2.65

It can be seen from Table 2 that the couplers of the invention exhibit high color-forming properties. It is also apparent from Examples 1 and 2 that the couplers of the invention have good solubility.

## CLAIMS

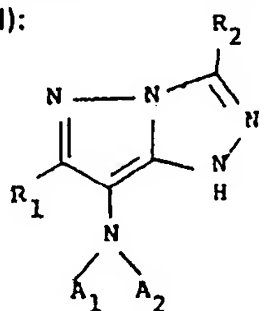
1. A color photographic silver halide light-sensitive material, comprising:  
a support base having thereon;  
a silver halide emulsion layer; and  
a 1H-pyrazolo [3-2-C]-S-triazole type of two equivalent magenta coupler, the coupler including a group which is released on coupling, the group being positioned on the coupler where the coupler undergoes a coupling reaction with an oxidized product of a developing agent, the group being represented by the general formula (I):



(I)

wherein  $A_1$  and  $A_2$  independently represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an acyl group, a sulfonyl group, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group or an aryloxy carbonyl group, provided both of  $A_1$  and  $A_2$  are not hydrogen atoms;  $A_1$  and  $A_2$  may combine together in combination with a nitrogen atom to form a 5- or 6-membered ring which may further condense with a benzene ring or a heterocyclic ring.

2. A color photographic silver halide light-sensitive material as claimed in Claim 1, wherein the coupler is represented by the general formula (II):



wherein  $A_1$  and  $A_2$  are defined in Claim 1 and  $R_1$  and  $R_2$  independently represent a hydrogen atom, an alkyl group, an aryl group, a heterocyclic group, an acylamino group, an alkylamino group, an anilino group, an alkoxy carbonyl group and an alkylthio group, provided both of  $R_1$  and  $R_2$  are not hydrogen atoms.

3. A color photographic silver halide light-sensitive material as claimed in Claim 1 or 2, wherein the  
5 coupler is present in an amount in the range of  $2 \times 10^{-3}$  to  $5 \times 10^{-1}$  mol per mol of silver. 5

4. A color photographic silver halide light-sensitive material as claimed in Claim 3, wherein the coupler is present in an amount in the range of  $1 \times 10^{-2}$  to  $5 \times 10^{-1}$  mol per mol of silver.

5. A color photographic silver halide light-sensitive material as claimed in any preceding claim, wherein  $A_1$  and  $A_2$  together form a 5- or 6-membered ring to which a benzene ring may be fused.

10 6. A color photographic silver halide light-sensitive material as claimed in Claim 1, wherein said coupler is any of Couplers 1 to 23 shown hereinbefore. 10

7. A color photographic silver halide light-sensitive material as claimed in Claim 1, substantially as hereinbefore described with reference to any of Film A of Example 1, the films of Example 2 or Films D to N of Examples 3 and 4.

15 8. A color photograph made by imagewise exposure and color development of a photographic material as claimed in any preceding claim. 15